



Infrared-laser-induced unimolecular reactions

The absorption of 30 or more infrared photons can raise a molecule into a highly excited vibrational state, leading to some intriguing problems in physical chemistry, quantum electronics and statistical mechanics.

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Photochemistry, which deals with the way in which chemical reactions are induced or altered by the presence of photons, has been a very active branch of science for many years. Although visible and ultraviolet photons, by giving rise to excited electronic states, have the most pronounced effects, much attention in recent years has gone to infrared photochemistry. Molecules irradiated with a powerful electromagnetic wave in the infrared remain in the electronic ground state (in the Born-Oppenheimer sense), but their vibrational modes may become highly excited. As a result, infrared-laser radiation often profoundly affects chemical reaction rates.

Several reviews of this topic have appeared recently.^{1,2} In this article we will restrict the subject further by the condition that the molecule absorbing the infrared radiation undergoes no collisions of any kind. Therefore our "universe" will be restricted to one single molecule and a large bath of infrared photons, supplied by one or more monochromatic lasers. This limited physical system is suitable for the study of intriguing questions in statistical mechanics, quantum electronics and physical chemistry.

Laser chemistry

It has been firmly established during the past few years that many polyatomic molecules can absorb sufficient energy from an intense infrared laser pulse that a true unimolecular reaction takes place. Because a chemical activation energy is typically about 3 eV and the infrared photon for the CO₂-laser wavelength near 10 microns is about 0.1 eV, the molecule is absorbing 30 or more photons.

Figure 1 illustrates the most studied

unimolecular reaction induced by infrared radiation, the dissociation of SF₆; this molecule is becoming the "hydrogen atom" for multiphoton chemistry and vibrational spectroscopy. The table on page 26 presents an incomplete list of the many polyatomic molecules that exhibit infrared-induced unimolecular reactions. The list is being augmented with each passing day. Large organic molecules are particularly favorable candidates for unimolecular infrared photochemistry.

The interest in the field was greatly enhanced by the discovery of R. V. Ambartsumian and Vladilen Letokhov that the laser-induced dissociation reaction is isotope selective.³ This, of course, has whetted the appetite of photochemists. They are excited by possible applications in the dissociation, cleavage, isomerization and synthesis of complex molecules, let alone the question of isotope selectivity. They are also led to the hope for bond-selective chemistry. Consider, for example, the halogen-substituted methane molecule CHFCIBr. With an infrared wavelength exciting the C-H vibration they might hope to eject the H atom and obtain the CFCIBr radical; with infrared wavelengths corresponding to the C-F, C-Cl and C-Br bonds, the other three respective dissociation channels might be activated. However, the realization of such dreams has proven more difficult than expected; we will discuss the reasons for this below.

From the physicist's point of view the system of one isolated molecule and a bath of monochromatic infrared photons is an intriguing one. What type of nonlinear optical effect could be responsible for the absorption of 30 or more infrared quanta? Does the energy remain in one mode, or will it be transferred to and shared with other modes? If so, will the distribution be statistical, and could the molecular behavior be ergodic—and on what time scale?

That these questions are nontrivial can be seen from the fact that a collisionless polyatomic molecule has only a few degrees of freedom, hardly the size of the systems to which statistical mechanics is usually applied. Nevertheless, we shall find below that statistical theory may give a good description of molecular behavior. How few degrees of freedom may a molecule have and still be capable of a statistical description? Will the dividing line occur for tri-atoms or quadra-atoms? This paper discusses these questions, but it remains for future work to provide definitive answers.

Experimental methods and results

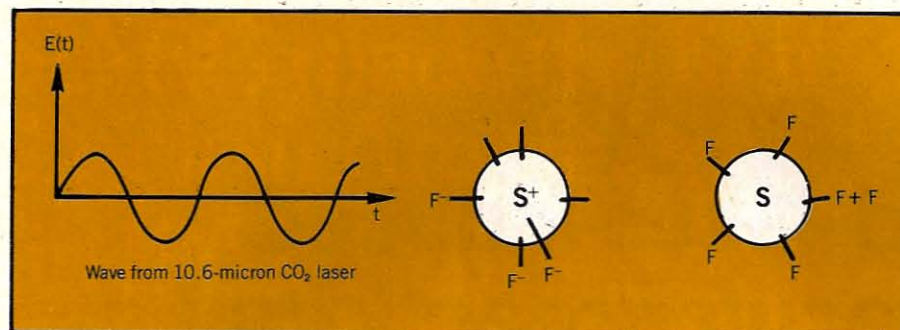
Before the advent of powerful infrared lasers, highly excited vibrational states could only be reached by thermal-equilibrium heating, by chemical activation or by electronic excitation. With short CO₂-laser pulses from TEA lasers, we can now excite individual molecules in a time that is short compared to any collision time.

Figure 2 shows the frequency dependence of the dissociation probability as determined by Ambartsumian and Letokhov.¹ The isotope selectivity follows immediately from the 17 cm⁻¹ shift in the infrared spectrum due to the mass difference between S³²F₆ and S³⁴F₆.

A key parameter of the multiphoton excitation process is the mean number of photons absorbed per molecule, $\langle n \rangle$. This quantity may be deduced from the direct attenuation of the laser beam⁴ or by the heat deposition, as determined with an acoustic calorimeter.⁵ If the excitation is strong enough, a fraction of the molecules may gain sufficient energy for dissociation. The reaction products may be analyzed by infrared spectroscopy, gas chromatography or mass spectroscopy.

The reaction yield is a rough measure of the tail of the molecular energy distribution, the fraction of molecules with

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Dissociation of sulfur hexafluoride by absorption of infrared radiation in the ν_3 vibrational mode, in which the positively charged sulfur atom moves with respect to the octahedron of the negatively charged F atoms. The structure of SF_6 is schematic. Figure 1

sufficient energy for dissociation. Figure 3 plots the reaction yield versus the mean excitation (n). Because $\langle n \rangle$ corresponds to the "center of gravity" of the population distribution over energy, this figure is probably the best available experimental measure for the shape of the energy distribution function. It compares the experimental points for two pulse durations with the theoretical curve calculated for a thermal distribution.

Collisionless dissociation occurs most convincingly at the intersection of a molecular beam with the laser beam;⁶ it is also firmly established by experiments with very short pulses in cells at low

pressure.⁷ Alternatively, the reaction products may be probed, with good time resolution, by resonance fluorescence excitation by a frequency-doubled dye laser.⁸ Figure 4, obtained by this technique, shows the population distribution over internal vibrational energy of the CF_2 fragments produced in the dissociation of CF_2Cl_2 .

Some of the other important experimental methods for studying these multiphoton reactions are:

- ▶ Ultraviolet and visible luminescence from electronically excited radicals created in the unimolecular reaction.⁹
- ▶ Infrared luminescence from bimolec-

ular reaction products of dissociation fragments with buffer-gas molecules.¹⁰

- ▶ Center-of-mass distribution of the kinetic energy of fragments created by dissociation in a molecular beam.^{7,11}
- ▶ Intramolecular isotopic branching ratio.¹²

These reactions also may be studied with double or multiple frequencies, and as a function of such parameters as laser frequency, laser intensity, pulse duration, gas pressure and delay time between pulses. Rather than compile and critically review this large body of experimental results here, we shall discuss the theoretical concepts that are consistent with the dominant experimental features of collisionless dissociation induced by infrared radiation.

The quasicontinuum

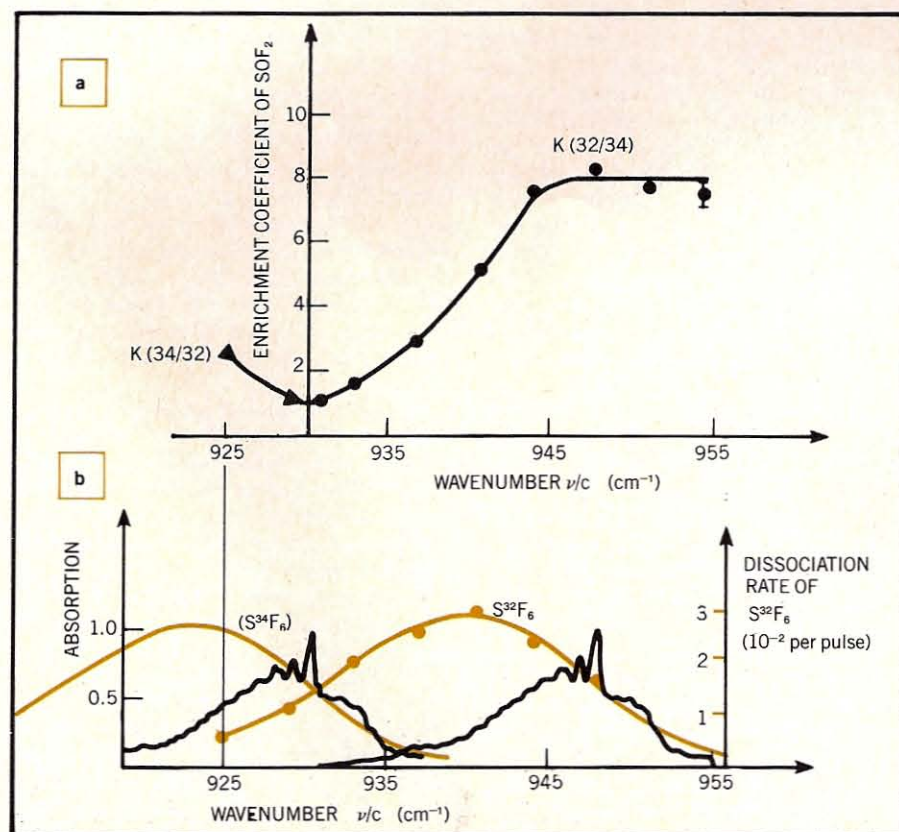
A diatomic molecule may be excited from the ground state to its first vibrational level by a resonant infrared photon. In general, the vibrational anharmonicity will necessitate a lower frequency for the absorption of a second photon, a still lower one for the third photon, and so on. To reach a level, $\nu = 30$, corresponding to a typical dissociation energy, 29 different frequencies therefore appear to be required. While available evidence suggests that indeed many selected infrared frequencies would be necessary to dissociate such a *diatomic* molecule, the situation in *polyatomic* molecules is qualitatively different.

One way to approach the problem of the polyatomic molecule is to imagine making an exact solution of the time-dependent Schrödinger equation for it. The initial condition would simply be the room-temperature canonical ensemble: a distribution of angular-momentum quantum numbers, internal vibrational energies and center-of-mass velocities. A solution of the time-dependent Schrödinger equation would require a knowledge of the energy, matrix elements, selection rules and exact wave function for each level up to the dissociation energy—an all-but-impossible task. Account would have to be taken of the octahedral splittings,¹³ rotational energy changes and Coriolis coupling, which tend to compensate the anharmonicity.^{1,2,14}

Fortunately, a simplification occurs. A schematic picture of the energy levels is shown in part a of figure 5. Each of the levels represents a specific vibrational-rotational state in the ground electronic manifold. The most important feature is the existence of several vibrational degrees of freedom.

In polyatomic molecules the density of states grows rapidly with energy E , due to the rapid expansion in the volume of accessible phase space. The number of possible permutations and combinations of vibrational modes increases rapidly with available energy.

The key point is that at a sufficiently



Laser isotope separation, based on the frequency dependence of the multiphoton dissociation of S^{32}F_6 and S^{34}F_6 by a CO_2 -laser pulse. Curve a shows the variation of enrichment coefficients $K(32/34)$ and $K(34/32)$ as points $\bullet$ and $\blacktriangle$ respectively. Curves b show (in color) the dissociation probability for the two isotopes and for comparison (in black) the respective linear absorption spectra. (After R. V. Ambartsumian and V. S. Letokhov, reference 1.) Figure 2

high density of states the "Golden Rule," as Enrico Fermi called it, becomes valid. In it the transitions are described in terms of constant rates, and the full Schrödinger equation reduces to a set of rate equations. This criterion determines the energy region we call the *quasicontinuum* to distinguish it from the *discrete levels*, where the full machinery of the Schrödinger equation is required. The two regions are labelled in figure 5 (part a). The quasicontinuum has now become accessible to investigation by infrared laser spectroscopy.

The basic condition for the validity of the Golden Rule is that the transition rate should be neither too fast nor too slow:

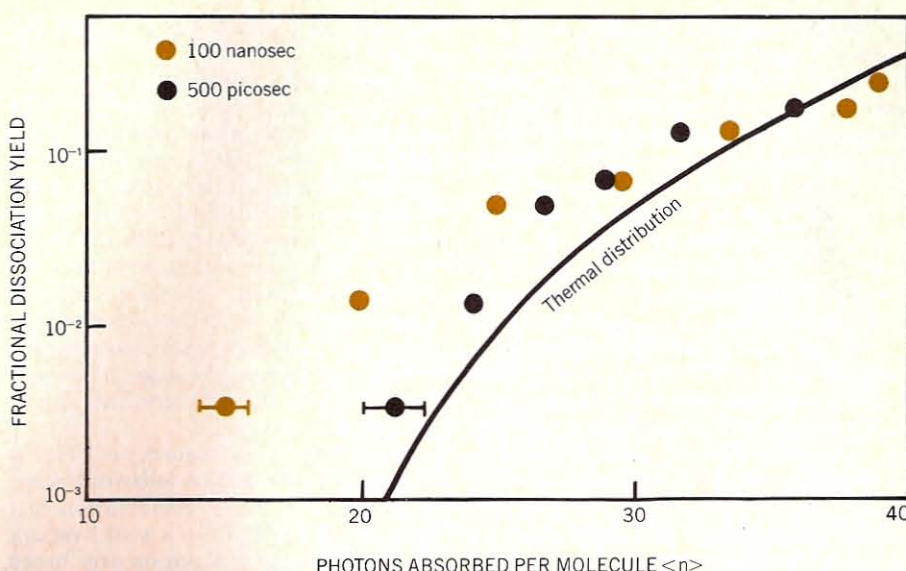
$$[\hbar\sigma(E)]^{-1} \ll \text{transition rate} \ll T_2^{-1} \quad (1)$$

where $\sigma(E)$ is the density of available states and $\hbar/T_2$ is the width of the distribution of oscillator strength. When $\sigma(E)$ is large enough, a rate-equation description is possible. This conclusion is especially useful in large polyatomics, where the thermal energy at room temperature is sufficient to boost most of the molecules into the quasicontinuum. In that instance, from the initial condition onward, we may use a rate-equation description¹⁵:

$$\frac{dW_n}{dt} = K_n^a I W_{n-1} + K_n^e I W_{n+1} - (K_{n+1}^a + K_{n-1}^e) I W_n - K_n^{\text{diss}} W_n \quad (2)$$

where W_n is the probability of being in that group of stationary states $n\hbar\omega$ above the starting level, K_n^a and K_n^e are absorption and stimulated-emission coefficients into that group, and K_n^{diss} is the reaction rate, which differs from zero only for those states above the activation energy. Because the rates, except for K_n^{diss} , are all proportional to the light intensity I , it may be divided from the right-hand side of equation 2 to show explicitly¹⁶ that the temporal evolution depends only on *intensity* $\times$ *time* = *energy fluence* (joules/cm²). This remarkable conclusion is confirmed by data of Paul Kolodner and his co-workers on the fractional dissociation of SF₆ as a function of pulse duration.⁷ The laser energy is held fixed as the peak power increases by a factor 200. The fraction dissociated increases only 30%, showing that it is almost independent of peak power. The reaction yields in infrared multiphoton dissociation depend very strongly on energy fluence but only weakly on peak power.

When a significant number of molecules have energy in excess of the chemical activation energy, the reaction rates on the right side of equation 2 becomes important. Even when a molecule has enough energy to react, it will not do so immediately. Only a small fraction of the available volume of the phase space leads to immediate chemical reaction—the molecule must wander through phase space for some time before encountering



The probability of dissociating a molecule with a laser pulse is a function of the mean energy of excitation per pulse, $\langle n \rangle \hbar\omega$. This graph gives information relating to the shape of the energy-distribution function for multiple photon absorption. The experimental points for two pulse durations, 100 nanosec and 500 picosec, are compared with a theoretical curve based on the assumption of a thermal equilibrium distribution of the same energy.

Figure 3

that small region. This is the essence of the RRKM (Rice-Ramsperger-Kassel-Marcus) theory of chemical reactions.¹⁷ The reaction rate is given by the fractional volume of phase space multiplied by a typical vibrational frequency ω_0 . In the simplest version, the Kassel model, the reaction rate is given by

$$\omega_0 \frac{n!(n-m+N-1)!}{(n-m)!(n+N-1)!}$$

where m is the minimum number of absorbed photons required for chemical reaction and N is the number of normal modes. The factorial coefficient estimates the fractional volume of phase space leading to immediate reaction. Typically, $m = 30$ and excess energy $n - m = 10$ leads to reaction within 10^{-7} sec. The excess kinetic energy of the reaction fragments has been measured,⁶ by Yuen Lee and Ron Shen and shown to be consistent with the RRKM theory.

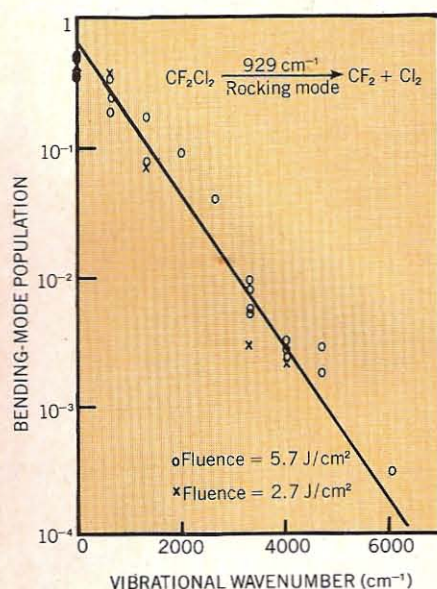
Before leaving this aspect, notice that n is not the quantum number of the driven normal mode, for example the ν_3 mode in SF₆. While the quantum states in the discrete region tend to be readily identifiable in terms of specific normal modes of the molecule, each individual state of the quasicontinuum is generally a superposition of all the modes. An up transition in n could mean either an up or down transition in ν_3 , depending on the individual states involved.

The intramolecular heat bath

The simplified picture implicit in equation 2 suggests that a quantum-mechanical basis set different from the energy eigenstates of the exact vibrational Hamiltonian might be appropriate. It is clear from the experimental observations that the energy originally fed into the ν_3

mode is at least partially distributed to other modes.

If we start with a very large molecule, we find a situation basically similar to that of spin relaxation in magnetic-resonance experiments. The radiation feeds energy into a transition between two (spin) energy levels, and a transfer to the continuum of energy levels of the lattice takes place with a characteristic relaxation rate T_1 .



The fraction of CF₂ photofragments $P(E_v)$ formed initially with vibrational energy E_v in the ν_2 bending mode from dissociating CF₂Cl₂. The pulses came from a CO₂ TEA laser operated at the frequency of the ν_8 rocking motion on CF₂Cl₂. The data points agree with the Planck distribution function for a vibrational temperature of 1050 K, shown by the straight line. (After D. S. King, J. C. Stephenson, ref. 8.)

Figure 4

Single out the vibrational transition at resonance and consider all other modes as the lattice or heat bath; this is certainly permissible in a large molecule at room temperature. The anharmonic coupling between the selected mode and all others provides a relaxation mechanism. It is perfectly feasible to heat a lattice by means of electronic paramagnetic resonance. Similarly, a large molecule may be heated by absorption on one infrared-active vibration. As the molecule heats up, the resonance frequency shifts and the relaxation time becomes shorter, just as an epr line may shift and broaden with increasing temperature. This description is consistent with the data of figure 6, showing the measured absorption spectrum of SF_6 that has been boosted into the quasicontinuum of energy levels by thermal heating in a shock tube.¹⁸ (For example, at 1000 K, SF_6 has thermal vibrational energy equivalent to 8000 cm^{-1} ,

high enough to put it into the quasicontinuum.)

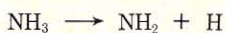
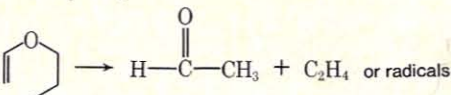
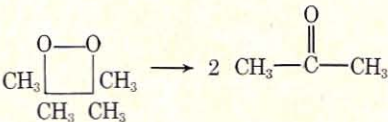
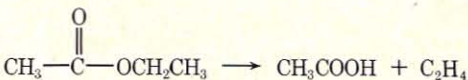
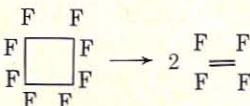
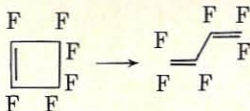
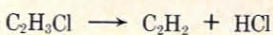
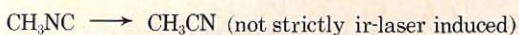
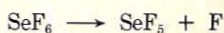
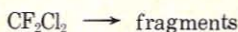
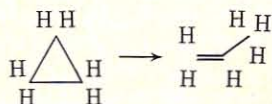
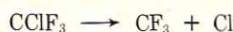
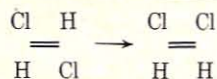
It may seem surprising that the rather sharp resonance of figure 6 would occur in an energy region we have been calling the quasicontinuum. The energy levels of the exact Hamiltonian are indeed closely spaced. Nevertheless, the oscillator strength for transitions from any given level of the quasicontinuum is not uniformly distributed, but tends to cluster near the frequencies of the normal modes. Since the ν_3 absorption band does remain reasonably narrow, the quasicontinuum transitions do indeed contribute to the isotopic selectivity.

Away from the ν_3 frequency of SF_6 , the absorption cross section falls off, but not to zero. The many combination and overtone bands produce a weak overlapping background absorption over broad regions of the infrared. The heating of the molecule makes available new com-

binations, further increasing the background absorption cross section, which is generally above 10^{-20} cm^2 . This explains the results of two-frequency irradiation experiments¹⁹ in which a heating pulse could be detuned from the main absorption line and still produce multiphoton excitation. At a cross section of 10^{-20} cm^2 an energy fluence of 100 J/cm^2 is more than sufficient to generate a chemical reaction. This also explains why the primary dissociation fragments⁶ are able to absorb more energy and undergo further fragmentation.

The internal molecular degrees of freedom are divided into two groups, the system and the heat bath. The driven, infrared-active, vibrational mode should be regarded as the *system*, with Hamiltonian $H_s(x)$ and wave functions $\psi_s(x)$. The other $N-1$ vibrational modes should be regarded as the *heat bath*, with Hamiltonian $H_b(y_1, y_2, \dots, y_{N-1})$ and wave

Unimolecular reactions induced by infrared multiphoton excitation



K. Nagai, M. Katayama, Chem. Phys. Lett. **51**, 329 (1977)

D. F. Dever, E. Grunwald, J. Am. Chem. Soc. **98**, 5055 (1976)

R. B. Hall, A. Kaldor, Bull. Am. Phys. Soc. **23**, 73 (1978)

A. T. Lin, A. M. Ronn, Chem. Phys. Lett. **49**, 255 (1977)

J. J. Tiee, C. Wittig, Appl. Phys. Lett. **32**, 236 (1978)

K. V. Ready, M. J. Berry, Chem. Phys. Lett. **52**, 111 (1977)

M. L. Lesiecki, W. A. Guillory, J. Chem. Phys. **66**, 4317 (1977)

K. R. Chien, S. H. Bauer, J. Phys. Chem. **80**, 1405 (1976)

F. M. Lussier, J. I. Steinfeld, Chem. Phys. Lett. **50**, 175 (1977)

A. Yegorov, R. M. J. Benmair, Chem. Phys. Lett. **46**, 290 (1977)

J. M. Preses, R. E. Weston Jr, G. W. Flynn, Chem. Phys. Lett. **46**, 69 (1977)

W. C. Danen, W. D. Munslow, D. W. Setser, J. Am. Chem. Soc. **99**, 6961 (1977)

Y. Haas, G. Yahov, Chem. Phys. Lett. **48**, 63 (1977)

R. N. Rosenfeld, G. I. Brauman, J. R. Barker, D. M. Golden, J. Am. Chem. Soc. **99**, 8063 (1977);
D. M. Brenner, private communication

J. D. Campbell, G. Hancock, J. B. Halpern, K. H. Welge, Opt. Commun. **17**, 38 (1976)

S. Bittenson, P. L. Houston, private communication

functions ψ_b . The system and heat bath are coupled by anharmonic terms in the molecular potential described by $V(x, y_1, \dots, y_{N-1})$. The total vibrational Hamiltonian is:

$$H = H_s(x) + V(x, y_1, \dots, y_{N-1}) + H_b(y_1, \dots, y_{N-1}) \quad (3)$$

where x and the y 's represent the phase-space coordinates of the system and the heat bath, respectively.

The new basis set consists of product wave functions of the form $\psi_s \psi_b$. The density-matrix equation of motion reduces to:

$$\frac{d\rho_s}{dt} = -\frac{i}{\hbar} [H_s, \rho_s] - \frac{i}{\hbar} [\mu \mathcal{E}, \rho_s] + \text{damping terms} \quad (4)$$

where ρ_s is the system density matrix and the "damping terms" refer to the T_1 - and T_2 -type relaxation rates, which are familiar from nuclear magnetic relaxation theory. A T_1 -type relaxation process is indicated in figure 5, part b. The driving Hamiltonian is the product of the dipole-moment operator μ and the laser field $\mathcal{E}$. The conditions for the validity of equation 4 are similar to those for equation 2:

$$\frac{1}{\hbar \sigma_b(E)} \ll \frac{1}{T_1} \leq \frac{1}{T_2} \ll \frac{1}{\tau_c} \quad (5)$$

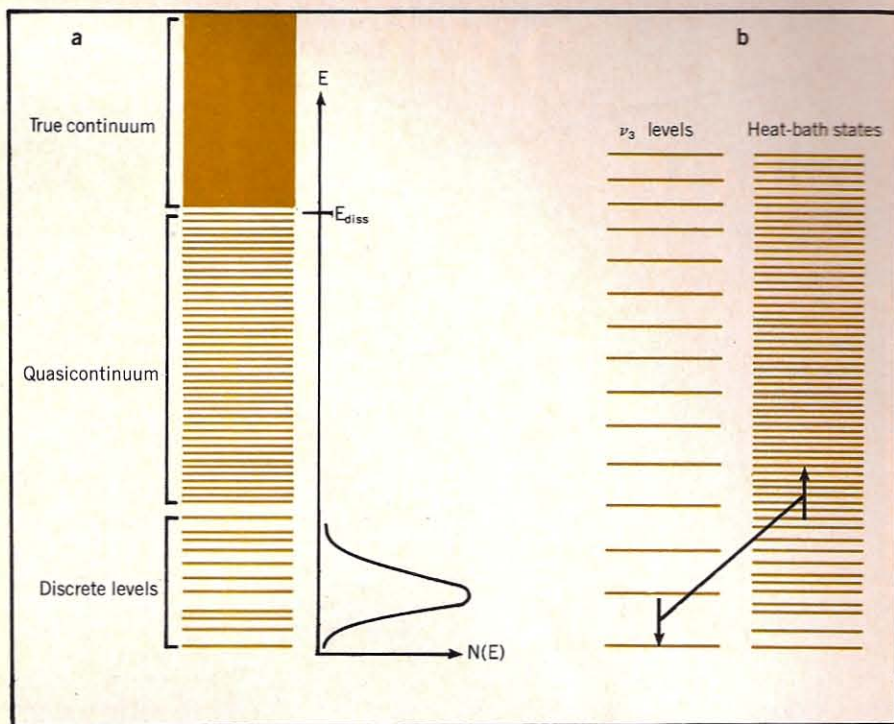
where $\sigma_b(E)$ is the heat-bath density of states and τ_c is the autocorrelation time of the fluctuating anharmonic potential, which is typically about one vibrational period. The anharmonic potential V determines T_1 and T_2 , and for $\tau_c \ll T_2$ the broadening is homogeneous. In nonrigid molecules, where slow internal motions are possible, τ_c could be much longer and the intramolecular damping could be partially inhomogeneous.

Intramolecular damping

Inhomogeneous contributions to the lineshape in addition to the intramolecular broadening are those from Doppler broadening, rotational structure and hot bands. Notice that these three inhomogeneous broadening mechanisms are associated with momentum, angular momentum and internal energy, respectively—the three conserved parameters of isolated systems. For $\hbar^{-1} |\mu \mathcal{E}| \ll T_2^{-1}$, the off-diagonal elements are small due to rapid dephasing, and the operator equation may be reduced to a set of rate equations for the populations:

$$\frac{dW_s}{dt} = [s\sigma(W_{s-1} - W_s) + (s+1)\sigma \times (W_{s+1} - W_s)] \frac{I}{\hbar \omega} + \text{damping} \quad (6)$$

where σ is the absorption cross section and $\hbar \omega$ is the infrared quantum. Although equation 6 resembles equation 2, the interpretation is different. The index s represents the quantum number of the



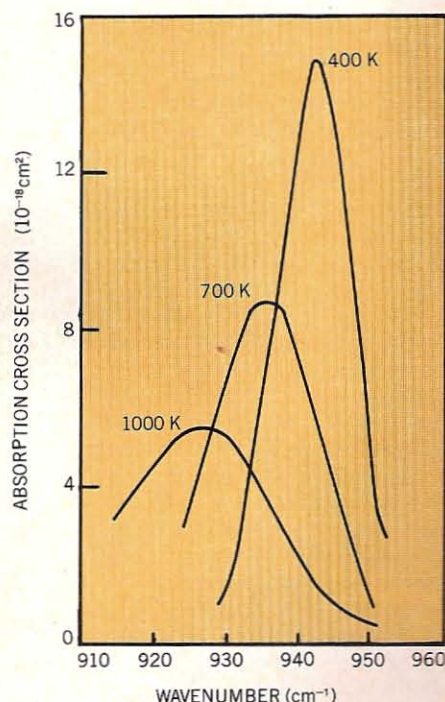
The true quantum states of the exact vibrational Hamiltonian. Diagram a shows the three regimes of vibrational excitation: discrete levels, quasicontinuum and true continuum. The initial population-distribution function $N(E)$ is the product of the vibrational density of states $\sigma(E)$ and the room-temperature Boltzmann factor. In the intramolecular-heat-bath picture, b, the energy levels of the infrared-active ν_3 mode are shown separately from the energy levels of the remaining modes, which form a quasicontinuous heat bath. Anharmonic coupling terms cause phase-fluctuation damping (with time constant T_2) and lifetime broadening (T_1) of the ν_3 mode. An energy relaxation process of the T_1 type is shown in black.

mode being driven, while n represents the total number of quanta in the molecule as a whole. For large molecules at sufficiently high temperature, most of the transitions take place between $s = 0$ and 1. This is because the energy is rapidly leaking out of the driven mode into the heat bath.

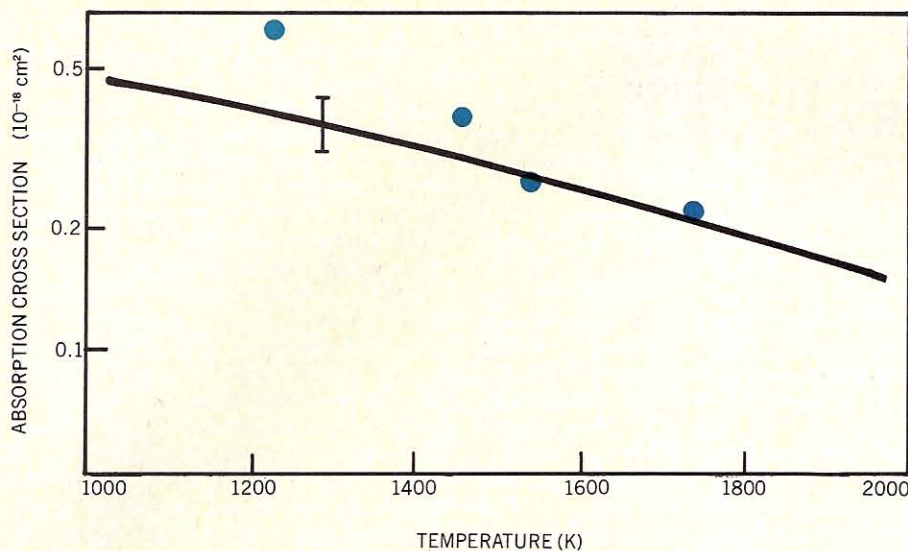
If the molecule is initially at absolute zero of temperature—that is, if there is no vibrational excitation—the concept of the heat bath is not valid for a one-photon transition. The molecule then must first undergo a multiphoton transition to a highly excited state with a sufficient admixture of other mode functions.

The SF_6 molecule at room temperature represents a borderline case. The discrete level transitions saturate, but for increasing intensity $|\mathcal{E}|^2$, multiphoton transitions to higher vibrational levels take place. Nature finds a ladder of nearly equally spaced energy levels with sufficient strength of connecting matrix elements to a level of excitation where conditions 1 or 5 are met. Thus the discrete levels represent a possible bottleneck, which becomes less important the higher the initial thermal excitation and the higher the laser intensity.

The subsequent vibrational heating of the molecule often causes a drop in the absorption cross section. Figure 6 shows that for SF_6 this is due to a shift and broadening of the ν_3 absorption band in



Absorption cross section per molecule in a thermal ensemble of SF_6 . At 1000 K the molecule is boosted into the quasicontinuum, but the ν_3 absorption feature remains well defined. The surprising sharpness of the resonance is due to the nonuniform distribution of oscillator strengths. Not shown is the background absorption of about 10^{-20} cm^2 . (A. V. Nowak, J. L. Lyman, ref. 18.)



Shock-tube absorption data (in color) are compared with the absorption cross section derived from CO₂-laser heating with 500-picosecond pulses as a function of vibrational excitation (black line); both are at 944 cm⁻¹. The two heating methods give similar results. Figure 7

the quasicontinuum—as opposed to a true saturation effect, which would occur between isolated levels in discrete regions. By employing a 500-picosec laser pulse of high peak power, the molecule may be boosted directly into the quasicontinuum, avoiding the saturation and bottlenecks effects in the discrete levels. Thus, the quasicontinuum absorption cross section should be similar for both laser-heated and shock-heated SF₆. The comparison, made in figure 7, shows good agreement in the temperature range above 1000 K.

In general, rate equations 2 or 6 can be solved numerically.¹⁵ For the case of constant cross section there exists an analytical solution—simply a Planck distribution.²⁰ If the T_1 relaxation rate to the heat bath is faster than the rate of heating, the heat bath will come into thermal equilibrium with the driven mode. The molecule as a whole will have a canonical thermal distribution, which tends, of course, to be peaked at a relatively well defined energy.

If the cross section decreases as the bath heats up, the population distribution will tend to pile up at higher energies and be somewhat narrower than thermal.¹⁵ In a realistic estimate of the population distribution, however, the effects of the discrete level barrier for entering the quasicontinuum must be accounted for. Inhomogeneous effects in the discrete level region tend to slow the energy deposition and smear out the population distribution.

As discussed earlier, a plot of reaction yield versus $\langle n \rangle$ is probably our best experimental measure of the shape of the population distribution. Figure 3 compares the experimental results with a thermal model. A 100-nanosec CO₂ laser pulse produces a significant yield even when the mean number of photons absorbed $\langle n \rangle$ is relatively low. The distri-

bution therefore tends to have a long high-energy tail and be broader than thermal. The distribution produced by a 500-picosec pulse, on the other hand, tends to be much closer to thermal, because the discrete level barrier plays a smaller role.

Another theoretical approach to the multiphoton chemistry problem is to treat the motion of the atoms in a purely classical manner, by making assumptions about the internuclear potential surface and effective charges as a function of internuclear distances. A Monte-Carlo type of calculation for various initial conditions of nuclear positions and velocities yields the required distributions and dissociation rates.²¹

Ergodicity

Chemists dream of being able to heat one part of a molecule while leaving the rest of the molecule relatively cold. Then a unimolecular reaction could be produced via a channel different from the thermodynamically favored one. Such a process was described above for the model molecule CHFClBr. In principle, this process would be possible if the rate of heating of a given vibrational mode could exceed $1/T_1$, the rate of relaxation to the rest of the molecule. This might be called mode-selective or bond-selective heating. In this situation, T_1 can be thought of as the time required to establish ergodicity.

Much fundamental work in statistical mechanics has concentrated on establishing the criteria under which ergodicity holds. (Inequality 5 is not such a condition; it merely determines whether the damping may be regarded as occurring at a constant rate, but it does not say whether the final steady state will be ergodic.) Perhaps the theoretical emphasis should shift to concentrate more effort on

$1/T_1$, the rate at which the equilibrium condition is approached.

Very little is known about the time constant T_1 . Numerical classical-trajectory calculations²¹ appear to show that T_1 can be less than 1 picosec. On the experimental side, there is also very little information. In an ingenious set of chemical-kinetics experiments, the intramolecular relaxation time was measured²² indirectly, by varying a buffer-gas pressure. For the cases studied the upper limit was estimated to be on the order of picoseconds.

In another approach, the excitation of the infrared-active ν_4 mode by multiphoton pumping of SF₆ in the ν_3 line was detected²³ by means of a weak ir fluorescence in the ν_4 band of frequencies. Due to the technological constraints it was only possible to establish an upper limit of 1 microsec on the time required to transfer energy into the ν_4 mode.

In an important experiment J. P. Maier and collaborators²⁴ employed picosecond infrared pulses to probe the redistribution of energy within the huge coumarin-6 molecule. They placed an upper limit of 4 psec on the T_1 lifetime of the molecule in the vapor phase at 305°C. It would be especially interesting to repeat this type of experiment in a smaller molecule with less thermal energy. Because a knowledge of T_1 under a variety of different conditions is essential for mode-selective chemistry, more quantitative answers will likely be forthcoming in the next few years.

Related questions are addressed by overtone spectroscopy in polyatomic molecules, where high vibrational levels are excited by means of a very weak single-photon absorption rather than multiphoton absorption. Figure 8 shows the spectrum of the fifth overtone band of the C-H stretch in benzene in the gas phase,²⁵ as obtained by a laser-acoustic technique, which is also illustrated by the photograph on the cover of this issue of PHYSICS TODAY.

To find such a sharp structure in the quasicontinuum should be no surprise to us by now. This has been understood by chemists in terms of a local-mode picture,²⁶ which is somewhat analogous to the heat-bath approach we have been using.

For the conditions of excitation in figure 8, the Doppler, rotational and hot-band broadening effects are negligible, and the broadening must arise mainly from the intramolecular anharmonic potential V . At present, the relative contributions of T_1 lifetime broadening and T_2 phase fluctuation broadening are unknown. The fifth overtone is a rather precise Lorentzian, while the fourth overtone has some substructure.²⁵ It is still too early to interpret this in terms of the onset of ergodicity at a definite energy level.

The infrared lineshapes in large poly-

atomic molecules are an interesting problem in their own right. These line profiles are usually observed in the liquid phase, in which strong solvent interactions obviously contribute to the line-shape. But the lines have similar broad shapes in the gas phase, as shown by figures 6 and 8. Until now only the three inhomogeneous effects, Doppler, rotational and hot-band broadening, were held responsible. The significance of fluctuations in the intramolecular anharmonic potential V for line broadening is now beginning to be recognized. Future developments will be quite fascinating as we learn to distinguish T_1 lifetime effects, T_2 phase-fluctuation effects, and in nonrigid molecules the effects of slow fluctuations.

Opportunities in chemical physics

We have already alluded to the potential applicability of infrared multiphoton chemistry in producing mode-selective chemical reactions. The pumping rate must be made high enough to compete with T_1 . In addition, the rise time of the pulse must be short enough to prevent a premature nonselective reaction.²⁷ With T_1 as short as it is, these conditions will be difficult to achieve. The 30-picosec CO_2 laser pulses produced by optical free-induction decay²⁸ will probably play a role.

Mode-selective nonstatistical heating is only one possible application, but it may be difficult to achieve. A number of other unique attributes of multiphoton-induced chemistry present themselves, even under ergodic conditions:

► Multiphoton heating can be ultrafast, leading to a higher temperature than can be achieved otherwise. This would permit a high-energy reaction channel to compete more effectively with a low-energy channel. The relative yields of the different reaction products could be controlled in this way.

► Infrared multiphoton heating is collisionless, so unimolecular reaction channels can be made to compete more effectively with bimolecular or collisional channels.

► Most important, infrared laser heating can operate on one component of a mixture, leaving the other components cold.

The latter, of course, is the essence of the isotope-separation capability, but it has exciting chemical applications as well. For example, consider two sides, A and B, of a chemical reaction:



By heating one of the components of A, it is possible to shift the equilibrium to the right, and vice versa for B. This might be rather useful in organic synthesis. Very frequently the challenge to the synthetic chemist is not in creating a molecule of a given formula, which is relatively easy, but in producing that molecule in a desired structure or isomer, which can be

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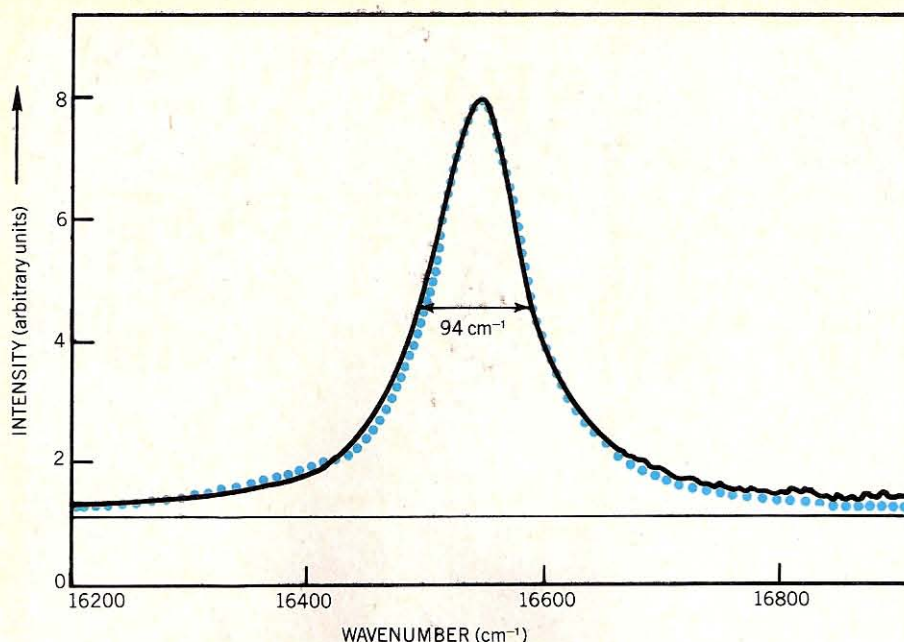
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The fifth-overtone absorption spectrum of the C-H stretching mode in benzene vapor. The linewidth is associated with intramolecular energy relaxation (T_1) and dephasing effects (T_2); the experiment is depicted on the cover. (After R. G. Bray, M. J. Berry, ref. 25.) Figure 8

much more difficult. The two isomers A and B will have rather different ir spectra. Irradiation at a wavelength at which the difference in absorption cross section is large can convert the molecules to the desired isomer.

There are many other ways to exploit the remarkable capability of heating one component of a mixture.

► Ultrapurification should be possible by selectively causing the undesired molecules to react.²⁹

► A high density of ground- or excited-state radicals can be generated by infrared photochemistry and employed as reagents.

► The laser can produce homogeneous catalysts, enhancing the speed of subsequent collisional reaction steps in a mixture.

One of the problems of infrared multiphoton heating is that it has been restricted mostly to the gas phase, although much interesting biological chemistry occurs in solution. The main hindering influence of the solvent is the strong relaxation, which tends to damp out the excitation and conduct away the heat. Again, ultrashort laser pulses should be able to overcome this effect and open the liquid phase to the prospect of ir photochemistry.

Challenges ahead

The infrared multiphoton excitation process will provide problems and opportunities for some time to come. In this review we have attempted to organize a conceptual framework upon which a quantitative understanding can be built. For example, at the present time the contributions of the various line-broadening mechanisms are unknown, even for

SF₆, the most studied case. Different types of molecular systems clearly will have to be studied in their own right; this will represent an important opportunity for specialists in nonlinear spectroscopy. The direct measurement of reliable T_1 relaxation times is an important challenge to picosecond spectroscopists.

The area of chemical applications is wide open and being pursued by many different groups. The results are still somewhat confusing, and it may take a while before we can make intelligent use of the tools that have become available.

In the area of fundamental statistical mechanics, the rate of approach toward ergodic behavior may turn out to be a more interesting question than whether true ergodicity is ultimately achieved. Theoretical calculations of T_1 in different situations would be very welcome. It will be interesting to learn whether an isolated triatomic molecule still falls within the realm of statistical theory!

* * *

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References

1. R. V. Ambartsumian, V. S. Letokhov, in *Chemical and Biochemical Applications of Lasers*, volume 3 (C. B. Moore, ed.), Academic, New York (1977), chapter 2; *Comm. At. Mol. Phys.* **6**, 13 (1976); V. S. Letokhov, *PHYSICS TODAY*, May 1977, page 23.
2. C. D. Cantrell, S. M. Freund, J. L. Lyman, in *Laser Handbook* (M. Stiche, ed.), North-Holland, New York (1978), volume 3.
3. R. V. Ambartsumian, V. S. Letokhov, E. A. Ryabov, N. V. Chekalin, *JETP Lett.* **20**,

- 273 (1974); J. L. Lyman, R. V. Jensen, J. Rink, C. P. Robinson, S. D. Rockwood, *Appl. Phys. Lett.* **27**, 87 (1975).
4. D. O. Ham, M. Rothschild, *Opt. Lett.* **1**, 28 (1977).
5. T. F. Deutsch, *Opt. Lett.* **1**, 25 (1977).
6. M. J. Coggiola, P. A. Schulz, Y. T. Lee, Y. R. Shen, *Phys. Rev. Lett.* **38**, 17 (1977); E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz, Y. R. Shen, *Chem. Phys. Lett.* **52**, 595 (1977).
7. P. Kolodner, C. Winterfeld, E. Yablonovitch, *Opt. Commun.* **20**, 119 (1977).
8. D. S. King, J. C. Stephenson, *Chem. Phys. Lett.* **51**, 48 (1977).
9. N. R. Isenor, R. V. Merchant, R. S. Hallsworth, M. C. Richardson, *Can. J. Phys.* **51**, 1281 (1973).
10. J. M. Preses, R. E. Weston Jr, G. W. Flynn, *Chem. Phys. Lett.* **48**, 425 (1977); C. R. Quick Jr, C. Wittig, *Chem. Phys. Lett.* **48**, 420 (1977).
11. K. L. Kompa, in *Tunable Lasers and Applications* (A. Mooradian, T. Jaeger, P. Stokseth, eds.), Springer, New York (1976).
12. S. W. Benson, A. J. Colussi, R. J. Hwang, J. J. Tice, *Chem. Phys. Lett.* **52**, 349 (1977).
13. C. D. Cantrell, H. W. Galbraith, *Opt. Commun.* **18**, 513 (1976).
14. N. Bloembergen, C. D. Cantrell, D. M. Larsen, in *Tunable Lasers and Applications* (A. Mooradian, T. Jaeger, P. Stokseth, eds.), Springer, New York (1976).
15. E. R. Grant, P. A. Schulz, A. S. Sudbo, Y. T. Lee, *Phys. Rev. Lett.* **40**, 115 (1978).
16. J. G. Black, E. Yablonovitch, N. Bloembergen, S. Mukamel, *Phys. Rev. Lett.* **38**, 1131 (1977).
17. P. J. Robinson, K. A. Holbrook, *Unimolecular Reactions*, Wiley, New York (1972).
18. A. V. Nowak, J. L. Lyman, *J. Quant. Spec. Rad. Trans.* **15**, 1945 (1975).
19. R. V. Ambartsumian, G. N. Makarov, A. A. Puresky, in *Laser Spectroscopy III* (J. L. Hall, J. L. Carlsten, eds.), Springer, New York (1977), page 76.
20. E. W. Montroll, K. E. Shuler, *J. Chem. Phys.* **26**, 454 (1957).
21. D. W. Noid, M. L. Koszykowski, R. A. Marcus, J. D. Macdonald, *Chem. Phys. Lett.* **51**, 540 (1977).
22. J. D. Rynbrandt, B. S. Rabinovitch, *J. Phys. Chem.* **75**, 2164 (1971).
23. D. S. Frankel, J. T. Manuccia, *Chem. Phys. Lett.*, to be published.
24. J. P. Maier, A. Seilmeier, A. Laubereau, W. Kaiser, *Chem. Phys. Lett.* **46**, 527 (1977).
25. R. G. Bray, M. J. Berry, in *Proceedings of the Conference on the Chemical Application of Lasers*, University of North Carolina, Chapel Hill (1977).
26. R. L. Swofford, M. S. Burberry, J. A. Morrell, A. C. Albrecht, *J. Chem. Phys.* **66**, 5245 (1977).
27. E. Yablonovitch, *Optics Lett.* **1**, 87 (1977).
28. E. Yablonovitch, J. Goldhar, *Appl. Phys. Lett.* **25**, 580 (1974); H. S. Kwok, E. Yablonovitch, *Appl. Phys. Lett.* **30**, 158 (1977).
29. J. H. Clark, R. G. Anderson, *Appl. Phys. Lett.* **32**, 46 (1978). □